Early-Stage Spinodal Decomposition in Ternary Blends Composed of a Random Copolymer and Homopolymers

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ABSTRACT: The Cahn−Hilliard−Cook (CHC) theory for ternary blends composed of an A−B random copolymer (A-r-B), an A homopolymer, and a B homopolymer is presented to investigate the dynamics of early-stage spinodal decomposition (SD). The cases for both fast theory and slow theory have been formulated. The time dependence of the structure factor of a ternary mixture is explored in the case when the mixture is quenched into both three-phase and two-phase regions. The time dependence of the structure factors of homopolymers A and B in the ternary blend is similar to those of binary homopolymer blends composed of A and B. The characteristic parameters of early-stage spinodal decomposition are formulated.

I. Introduction

Numerous studies have been reported on ternary blends consisting of two homopolymers (A and B) and the corresponding block copolymer (A−B), since the copolymer plays an important role not only as a compatibilizer, enhancing the miscibility of A/B blends, but also as a surfactant, reducing the interfacial tension between A-rich and B-rich regions.[1−6] Moreover, some studies[7−12] have theoretically explored the effects of the added A−B on the dynamics of the phase separation processes of A/B blends.

The ternary system focused on here consists of two homopolymers (A and B) and the corresponding random copolymer (A-r-B). Leibler[13] first investigated the phase diagram of the ternary system with A and B homopolymers and a random copolymer containing equal amounts of A monomer and B monomer by using the Flory−Huggins theory, where A, B, and A-r-B have the same polymerization index N. It was found that the ternary mixture should have a tricritical point and that its phase diagram is classified into four regions, depending on the Flory−Huggins segmental interaction parameter χ between A and B as shown in Figure 1. (i) In region I ($\chi N < 2$) (Figure 1a) the ternary mixture is homogeneous at all compositions. (ii) In region II ($2 < \chi N < 6$) (Figure 1b) the ternary mixture is separated into an A-rich region and a B-rich region and A-r-B is dissolved into both phases equally. There is only one critical point (point C). (iii) In region III ($6 < \chi N < 8$) (Figure 1c) the phase diagram contains three two-phase regions (HKIH, HJLH, and AIJBA) and one three-phase region (HIJH); two critical points (points K and L) of demixing exist. The three-phase region consists of an A-rich region, a B-rich region, and an A-r-B rich region. (iv) In region IV ($8 < \chi N$) (Figure 1d) as in the case of region III, the phase diagram contains three two-phase regions and one three-phase region (NOPN) but the critical points have disappeared.

Broseta and Fredrickson[14] investigated the molecular weight effects of a random copolymer on the phase diagram of a ternary system in which the two homopolymers have the same polymerization index N_H, which is different from the polymerization index N_R of a random copolymer having equal amounts of A monomer and B monomer. They found two different types of phase diagrams according to the polymerization index ratio $\alpha = N_H/N_R$ of the homopolymer to the random copolymer. If α is smaller than 2/5, the three-phase region emerges continuously via a tricritical point. Otherwise, the three-phase region appears discontinuously.

Our aim is to explore the dynamics of the phase separation process in ternary mixtures of A, B, and A-r-B quenched into the several regions classified by Leibler. In the present paper, as a first step, we formulated the Cahn−Hilliard−Cook (CHC) theory[15,16] to describe the early-stage spinodal decomposition (SD) and to investigate the time dependence of the structure factor of the ternary system using the Flory−Huggins−de Gennes theory for the free energy functional of mixing.

II. Theory

First, let us derive the basic equation describing the dynamics of early-stage SD in a ternary mixture of A, B, and A-r-B. Here $\phi_A(\mathbf{r},t)$, $\phi_B(\mathbf{r},t)$, and $\phi_R(\mathbf{r},t)$ denote, respectively, the volume fraction of A, B, and A-r-B at position $\mathbf{r}$ and time t. The continuity equations for A, B, and A-r-B components are given by

$$\frac{\partial \phi_A(\mathbf{r},t)}{\partial t} + \nabla \mathbf{J}_A(\mathbf{r},t) = 0 \quad (1)$$

$$\frac{\partial \phi_B(\mathbf{r},t)}{\partial t} + \nabla \mathbf{J}_B(\mathbf{r},t) = 0 \quad (2)$$

and

$$\frac{\partial \phi_R(\mathbf{r},t)}{\partial t} + \nabla \mathbf{J}_R(\mathbf{r},t) = 0 \quad (3)$$

where $\mathbf{J}_k$ is the flux of the kth component (k = A, B, or R). The Onsager theory gives the following relations

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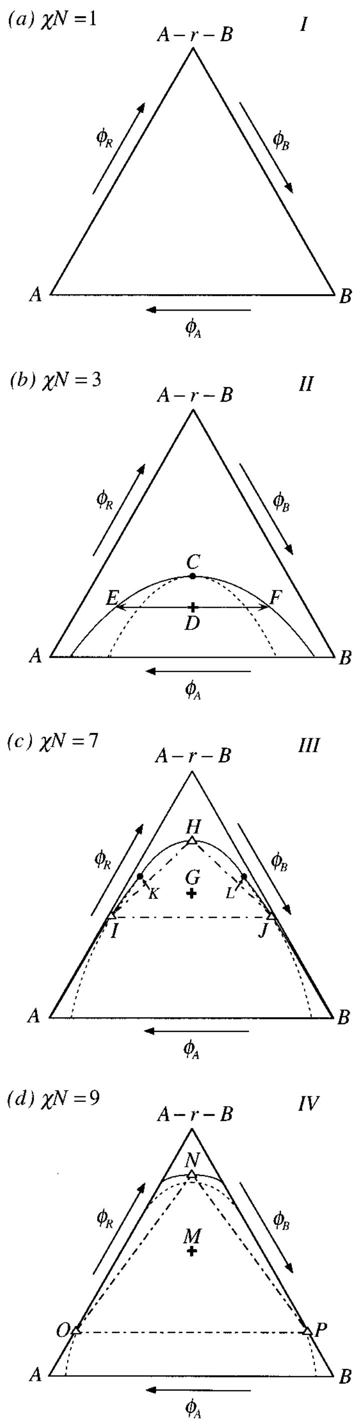

Figure 1. Phase diagram of A/B/A-r-B system at region I (a), region II (b), region III (c), and region IV (d). Binodal line and spinodal line are indicated by solid line and broken line, respectively. Point C in part b and points K and L in part c denote the critical point. In parts c and d, open triangles denote the equilibrium composition. The composition within the triangles (HIJ and NOP) is three-phase region.

between the flux and the chemical potential μ_k of the kth component:

$$\mathbf{J}_A = -\Lambda_{AA}\nabla(\mu_A - \mu_R) - \Lambda_{AB}\nabla(\mu_B - \mu_R) \qquad (4)$$

and

$$\mathbf{J}_B = -\Lambda_{BA}\nabla(\mu_A - \mu_R) - \Lambda_{BB}\nabla(\mu_B - \mu_R) \qquad (5)$$

where Λ_{ij} is the Onsager kinetic coefficient. It is noted that the thermal fluctuation effects[16] and the hydrodynamic interactions effects[17] are neglected in the above equations. Substituting eqs 1 and 2 into eqs 4 and 5, respectively, we obtain

$$\frac{\partial\phi_A(\mathbf{r},t)}{\partial t} = \nabla\Lambda_{AA}\nabla(\mu_A - \mu_R) + \nabla\Lambda_{AB}\nabla(\mu_B - \mu_R) \qquad (6)$$

and

$$\frac{\partial\phi_B(\mathbf{r},t)}{\partial t} = \nabla\Lambda_{BA}\nabla(\mu_A - \mu_R) + \nabla\Lambda_{BB}\nabla(\mu_B - \mu_R) \qquad (7)$$

According to the Flory−Huggins−de Gennes theory,[18] the free energy functional $F\{\phi_A,\phi_B,\phi_R\}$ per lattice site are given by

$$F\{\phi_A,\phi_B,\phi_R\}/k_BT = \frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B + \frac{\phi_R}{N_R}\ln\phi_R + \chi\phi_A\phi_B + (1-f)^2\chi\phi_A\phi_R + f^2\chi\phi_B\phi_R + \frac{a^2}{36}\sum_{k=A,B,R}\frac{1}{\phi_k}(\nabla\phi_k)^2 \qquad (8)$$

where k_B is the Boltzman constant, T the absolute temperature, χ the Flory−Huggins segmental interaction parameter between A and B, N_k the polymerization index of the kth component, f the volume fraction of A in the random copolymer, and a the statistical segment length. Here it is assumed that the statistical segment length of each component is identical. Note that we do not consider A-r-B by itself to show any microphase separation or form any mesophases. We, hence, treated the A-r-B as a homopolymer in eq 8. The validity of this treatment was proved by the experimental results on the scattered intensity of A-r-B/A blends in their one-phase region[19] and the phase separation process of A-r-B/A blends.[20] The standard definition of μ_k gives

$$\mu_k = F + \sum_{j=A,B,R}\frac{\delta F}{\delta\phi_j}(\delta_{kj} - \phi_j) \qquad (9)$$

where δ_{kj} is the Kronecker delta and hence

$$\mu_i - \mu_j = \frac{\delta F}{\delta\phi_i} - \frac{\delta F}{\delta\phi_j} \qquad (i,j = \text{A, B, or R}) \qquad (10)$$

For small concentration fluctuations, $\delta F/\delta\phi_i$ can be approximated by

$$\frac{\delta F}{\delta\phi_i} = \left.\frac{\delta F}{\delta\phi_i}\right|_{\phi} + \sum_{j=A,B,R}\left.\frac{\delta^2 F}{\delta\phi_i\delta\phi_j}\right|_{\phi}[\phi_j - \phi_{j,0}] \qquad (11)$$

where

$$\phi = (\phi_{A,0}, \phi_{B,0}, \phi_{R,0}) \qquad (12)$$

and $\phi_{k,0}$ is the space average of ϕ_k. Substituting eqs 10 and 11 into eqs 6 and 7, we obtain

$$\frac{\partial\phi_{\mathrm{A}}(\mathbf{r},t)}{\partial t} = \left[\Lambda_{\mathrm{AA}}\left(\frac{1}{N_{\mathrm{A}}\phi_{\mathrm{A},0}} + \frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} - \frac{1}{2}\chi\right) + \Lambda_{\mathrm{AB}}\left(\frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} + \frac{1}{2}\chi\right)\right]\nabla^2\phi_{\mathrm{A}}(\mathbf{r},t) - \left[\Lambda_{\mathrm{AA}}\left(\frac{a^2}{18\phi_{\mathrm{A},0}} + \frac{a^2}{18\phi_{\mathrm{R},0}}\right) + \Lambda_{\mathrm{AB}}\left(\frac{a^2}{18\phi_{\mathrm{R},0}}\right)\right]\nabla^4\phi_{\mathrm{A}}(\mathbf{r},t) + \left[\Lambda_{\mathrm{AA}}\left(\frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} + \frac{1}{2}\chi\right) + \Lambda_{\mathrm{AB}}\left(\frac{1}{N_{\mathrm{B}}\phi_{\mathrm{B},0}} + \frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} - \frac{1}{2}\chi\right)\right]\nabla^2\phi_{\mathrm{B}}(\mathbf{r},t) - \left[\Lambda_{\mathrm{AA}}\left(\frac{a^2}{18\phi_{\mathrm{R},0}}\right) + \Lambda_{\mathrm{AB}}\left(\frac{a^2}{18\phi_{\mathrm{B},0}} + \frac{a^2}{18\phi_{\mathrm{R},0}}\right)\right]\nabla^4\phi_{\mathrm{B}}(\mathbf{r},t) \tag{13}$$

and

$$\frac{\partial\phi_{\mathrm{B}}(\mathbf{r},t)}{\partial t} = \left[\Lambda_{\mathrm{BA}}\left(\frac{1}{N_{\mathrm{A}}\phi_{\mathrm{A},0}} + \frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} - \frac{1}{2}\chi\right) + \Lambda_{\mathrm{BB}}\left(\frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} + \frac{1}{2}\chi\right)\right]\nabla^2\phi_{\mathrm{A}}(\mathbf{r},t) - \left[\Lambda_{\mathrm{BA}}\left(\frac{a^2}{18\phi_{\mathrm{A},0}} + \frac{a^2}{18\phi_{\mathrm{R},0}}\right) + \Lambda_{\mathrm{BB}}\left(\frac{a^2}{18\phi_{\mathrm{R},0}}\right)\right]\nabla^4\phi_{\mathrm{A}}(\mathbf{r},t) + \left[\Lambda_{\mathrm{BA}}\left(\frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} + \frac{1}{2}\chi\right) + \Lambda_{\mathrm{BB}}\left(\frac{1}{N_{\mathrm{B}}\phi_{\mathrm{B},0}} + \frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} - \frac{1}{2}\chi\right)\right]\nabla^2\phi_{\mathrm{B}}(\mathbf{r},t) - \left[\Lambda_{\mathrm{BA}}\left(\frac{a^2}{18\phi_{\mathrm{R},0}}\right) + \Lambda_{\mathrm{BB}}\left(\frac{a^2}{18\phi_{\mathrm{B},0}} + \frac{a^2}{18\phi_{\mathrm{R},0}}\right)\right]\nabla^4\phi_{\mathrm{B}}(\mathbf{r},t) \tag{14}$$

Here Λ_{ij} are assumed to be independent of $\phi_k(\mathbf{r},t)$. The Onsager kinetic coefficient can be obtained from two different theories: the slow theory proposed by de Gennes[18,21] and the fast theory proposed by Kramer[22] and Brochard.[23] According to the slow theory, Λ_{ij} are given by (see Appendix)

$$\Lambda_{\mathrm{AA}} = \frac{\Lambda_{0,\mathrm{AA}}(\Lambda_{0,\mathrm{BB}} + \Lambda_{0,\mathrm{RR}})}{\sum_{k=\mathrm{A,B,R}}\Lambda_{0,kk}} \tag{15}$$

$$\Lambda_{\mathrm{BB}} = \frac{\Lambda_{0,\mathrm{BB}}(\Lambda_{0,\mathrm{AA}} + \Lambda_{0,\mathrm{RR}})}{\sum_{k=\mathrm{A,B,R}}\Lambda_{0,kk}} \tag{16}$$

and

$$\Lambda_{\mathrm{AB}} = \Lambda_{\mathrm{BA}} = \frac{-\Lambda_{0,\mathrm{AA}}\Lambda_{0,\mathrm{BB}}}{\sum_{k=\mathrm{A,B,R}}\Lambda_{0,kk}} \tag{17}$$

where $\Lambda_{0,kk}$ is the bare Onsager kinetic coefficient of k component and U is the potential determined by the incompressible condition. $\Lambda_{0,kk}$ is given by[21,24]

$$\Lambda_{0,kk}(q) = 6D_kN_k\phi_{k,0}\frac{1 - \exp(-N_ka^2q^2/6)}{N_ka^2q^2} \tag{18}$$

where D_k and q are, respectively, the self-diffusion coefficient of k component and the wavenumber.

On the other hand, the fast theory gives (see Appendix)

$$\Lambda_{\mathrm{AA}} = (1 - \phi_{\mathrm{A}})^2\Lambda_{0,\mathrm{AA}} + \phi_{\mathrm{A}}^2\Lambda_{0,\mathrm{BB}} + \phi_{\mathrm{A}}^2\Lambda_{0,\mathrm{RR}} \tag{19}$$

$$\Lambda_{\mathrm{BB}} = \phi_{\mathrm{B}}^2\Lambda_{0,\mathrm{AA}} + (1 - \phi_{\mathrm{B}})^2\Lambda_{0,\mathrm{BB}} + \phi_{\mathrm{B}}^2\Lambda_{0,\mathrm{RR}} \tag{20}$$

and

$$\Lambda_{\mathrm{AB}} = \Lambda_{\mathrm{BA}} = -\phi_{\mathrm{A}}(1 - \phi_{\mathrm{B}})\Lambda_{0,\mathrm{AA}} - (1 - \phi_{\mathrm{B}})\phi_{\mathrm{A}}\Lambda_{0,\mathrm{BB}} + \phi_{\mathrm{A}}\phi_{\mathrm{B}}\Lambda_{0,\mathrm{RR}} \tag{21}$$

In the present paper, we will use the slow theory, i.e., eqs 15−17. It is noted, however, that the results from the fast and slow theories become identical, i.e., eqs 15−17 become identical with eqs 19−21, respectively, in the case where $N_{\mathrm{A}} = N_{\mathrm{B}} = N_{\mathrm{R}}$ as in the systems to be treated in section III.

By applying the Fourier transform to eqs 13 and 14, we get

$$\frac{\partial\phi_{\mathrm{A}}(q,t)}{\partial t} = D_{11}(q)\phi_{\mathrm{A}}(q,t) + D_{12}(q)\phi_{\mathrm{B}}(q,t) \tag{22}$$

and

$$\frac{\partial\phi_{\mathrm{B}}(q,t)}{\partial t} = D_{21}(q)\phi_{\mathrm{A}}(q,t) + D_{22}(q)\phi_{\mathrm{B}}(q,t) \tag{23}$$

where

$$D_{11}(q) = -\left[\Lambda_{\mathrm{AA}}\left(\frac{1}{N_{\mathrm{A}}\phi_{\mathrm{A},0}} + \frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} - \frac{1}{2}\chi\right) + \Lambda_{\mathrm{AB}}\left(\frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} + \frac{1}{2}\chi\right)\right]q^2 - \left[\Lambda_{\mathrm{AA}}\left(\frac{a^2}{18\phi_{\mathrm{A},0}} + \frac{a^2}{18\phi_{\mathrm{R},0}}\right) + \Lambda_{\mathrm{AB}}\left(\frac{a^2}{18\phi_{\mathrm{R},0}}\right)\right]q^4 \tag{24}$$

$$D_{12}(q) = -\left[\Lambda_{\mathrm{AA}}\left(\frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} + \frac{1}{2}\chi\right) + \Lambda_{\mathrm{AB}}\left(\frac{1}{N_{\mathrm{B}}\phi_{\mathrm{B},0}} + \frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} - \frac{1}{2}\chi\right)\right]q^2 - \left[\Lambda_{\mathrm{AA}}\left(\frac{a^2}{18\phi_{\mathrm{R},0}}\right) + \Lambda_{\mathrm{AB}}\left(\frac{a^2}{18\phi_{\mathrm{B},0}} + \frac{a^2}{18\phi_{\mathrm{R},0}}\right)\right]q^4 \tag{25}$$

$$D_{21}(q) = -\left[\Lambda_{\mathrm{BA}}\left(\frac{1}{N_{\mathrm{A}}\phi_{\mathrm{A},0}} + \frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} - \frac{1}{2}\chi\right) + \Lambda_{\mathrm{BB}}\left(\frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} + \frac{1}{2}\chi\right)\right]q^2 - \left[\Lambda_{\mathrm{BA}}\left(\frac{a^2}{18\phi_{\mathrm{A},0}} + \frac{a^2}{18\phi_{\mathrm{R},0}}\right) + \Lambda_{\mathrm{BB}}\left(\frac{a^2}{18\phi_{\mathrm{R},0}}\right)\right]q^4 \tag{26}$$

and

$$D_{22}(q) = -\left[\Lambda_{\mathrm{BA}}\left(\frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} + \frac{1}{2}\chi\right) + \Lambda_{\mathrm{BB}}\left(\frac{1}{N_{\mathrm{B}}\phi_{\mathrm{B},0}} + \frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} - \frac{1}{2}\chi\right)\right]q^2 - \left[\Lambda_{\mathrm{BA}}\left(\frac{a^2}{18\phi_{\mathrm{R},0}}\right) + \Lambda_{\mathrm{BB}}\left(\frac{a^2}{18\phi_{\mathrm{B},0}} + \frac{a^2}{18\phi_{\mathrm{R},0}}\right)\right]q^4 \tag{27}$$

When eqs 22 and 23 are solved, the time dependence of structure factors $S_{\mathrm{AA}}(q,t)$, $S_{\mathrm{AB}}(q,t)$, and $S_{\mathrm{BB}}(q,t)$ are obtained:

$$S_{\mathrm{AA}}(q,t) = \frac{1}{(\lambda_1(q) - \lambda_2(q))^2}[a_1(q)\mathrm{e}^{2\lambda_1(q)t} + a_2(q)\mathrm{e}^{(\lambda_1(q)+\lambda_2(q))t} + a_3(q)\mathrm{e}^{2\lambda_2(q)t}] \tag{28}$$

$$S_{\mathrm{BB}}(q,t) = \frac{1}{(\lambda_1(q) - \lambda_2(q))^2}[b_1(q)\mathrm{e}^{2\lambda_1(q)t} + b_2(q)\mathrm{e}^{(\lambda_1(q)+\lambda_2(q))t} + b_3(q)\mathrm{e}^{2\lambda_2(q)t}] \tag{29}$$

and

$$S_{\mathrm{AB}}(q,t) = \frac{1}{(\lambda_1(q) - \lambda_2(q))^2}[c_1(q)\mathrm{e}^{2\lambda_1(q)t} + c_2(q)\mathrm{e}^{(\lambda_1(q)+\lambda_2(q))t} + c_3(q)\mathrm{e}^{2\lambda_2(q)t}] \tag{30}$$

with

$$a_1(q) = [\lambda_1(q) - D_{22}(q)]^2 S_{\mathrm{AA}}(q,0) + 2D_{12}(q)[\lambda_1(q) - D_{22}(q)]S_{\mathrm{AB}}(q,0) + D_{12}(q)^2 S_{\mathrm{BB}}(q,0) \tag{31}$$

$$a_2(q) = [\lambda_1(q) - D_{22}(q)][D_{22}(q) - \lambda_2(q)]S_{\mathrm{AA}}(q,0) + D_{12}(q)[2D_{22}(q) - \lambda_1(q) - \lambda_2(q)]S_{\mathrm{AB}}(q,0) - D_{12}(q)^2 S_{\mathrm{BB}}(q,0) \tag{32}$$

$$a_3(q) = [D_{22}(q) - \lambda_2(q)]^2 S_{\mathrm{AA}}(q,0) - 2D_{12}(q)[D_{22}(q) - \lambda_2(q)]S_{\mathrm{AB}}(q,0) + D_{12}(q)^2 S_{\mathrm{BB}}(q,0) \tag{33}$$

$$b_1(q) = [\lambda_1(q) - D_{11}(q)]^2 S_{\mathrm{BB}}(q,0) + 2D_{21}(q)[\lambda_1(q) - D_{11}(q)]S_{\mathrm{AB}}(q,0) + D_{21}(q)^2 S_{\mathrm{AA}}(q,0) \tag{34}$$

$$b_2(q) = [\lambda_1(q) - D_{11}(q)][D_{11}(q) - \lambda_2(q)]S_{\mathrm{BB}}(q,0) + D_{21}(q)[2D_{11}(q) - \lambda_1(q) - \lambda_2(q)]S_{\mathrm{AB}}(q,0) - D_{21}(q)^2 S_{\mathrm{AA}}(q,0) \tag{35}$$

$$b_3(q) = [D_{11}(q) - \lambda_2(q)]^2 S_{\mathrm{AA}}(q,0) - 2D_{21}(q)[D_{11}(q) - \lambda_2(q)]S_{\mathrm{AB}}(q,0) + D_{21}(q)^2 S_{\mathrm{BB}}(q,0) \tag{36}$$

$$c_1(q) = D_{21}(q)[\lambda_1(q) - D_{22}(q)]S_{\mathrm{AA}}(q,0) + \{[\lambda_1(q) - D_{11}(q)][\lambda_1(q) - D_{22}(q)] + D_{12}(q)D_{21}(q)\}S_{\mathrm{AB}}(q,0) + D_{12}(q)[\lambda_1(q) - D_{11}(q)]S_{\mathrm{AA}}(q,0) \tag{37}$$

$$c_2(q) = D_{21}(q)[D_{22}(q) - D_{11}(q)]S_{\mathrm{AA}}(q,0) + \{[D_{22}(q) - \lambda_2(q)]^2 + [\lambda_1(q) - D_{22}(q)]^2 - 2D_{12}(q)D_{21}(q)\}S_{\mathrm{AB}}(q,0) + D_{12}(q)[D_{11}(q) - D_{22}(q)]S_{\mathrm{BB}}(q,0) \tag{38}$$

and

$$c_3(q) = D_{21}(q)[\lambda_2(q) - D_{22}(q)]S_{\mathrm{AA}}(q,0) + \{[\lambda_2(q) - D_{11}(q)][\lambda_2(q) - D_{22}(q)] + D_{12}(q)D_{21}(q)\}S_{\mathrm{AB}}(q,0) + D_{12}(q)[\lambda_2(q) - D_{11}(q)]S_{\mathrm{AA}}(q,0) \tag{39}$$

where $S_{ij}(q,t)$ (i,j = A, B, or R) is defined by

$$S_{ij}(q,t) = \langle \phi_i(q,t)\phi_j^*(q,t)\rangle_T \tag{40}$$

with $\langle\ \rangle_T$ denoting a thermal average. $\lambda_1(q)$ and $\lambda_2(q)$ ($\lambda_1(q) > \lambda_2(q)$) are the solution of

$$(D_{11}(q) - \lambda(q))(D_{22}(q) - \lambda(q)) - D_{12}(q)D_{21}(q) = 0 \tag{41}$$

$S_{ij}(q,0)$ (i,j = A,B, or R) are the structure factors before the quench and given by[25-27]

$$S_{\mathrm{AA}}(q,0) = S^0_{\mathrm{AA}}(q)\left[(S^0_{\mathrm{BB}}(q) + S^0_{\mathrm{RR}}(q)) - \frac{1}{2}\chi_0 S^0_{\mathrm{BB}}(q)S^0_{\mathrm{RR}}(q)\right]/\Delta \tag{42}$$

$$S_{\mathrm{AB}}(q,0) = S^0_{\mathrm{AA}}(q)S^0_{\mathrm{BB}}(q)\left[-1 - \frac{1}{2}\chi_0 S^0_{\mathrm{RR}}(q)\right]/\Delta \tag{43}$$

and

$$S_{\mathrm{BB}}(q,0) = S^0_{\mathrm{BB}}(q)\left[(S^0_{\mathrm{AA}}(q) + S^0_{\mathrm{RR}}(q)) - \frac{1}{2}\chi_0 S^0_{\mathrm{AA}}(q)S^0_{\mathrm{RR}}(q)\right]/\Delta \tag{44}$$

where

$$S^0_{\mathrm{AA}}(q) = \left[\frac{1}{N_{\mathrm{A}}\phi_{\mathrm{A},0}} + \frac{a^2q^2}{18\phi_{\mathrm{A},0}}\right]^{-1} \tag{45}$$

$$S^0_{\mathrm{BB}}(q) = \left[\frac{1}{N_{\mathrm{B}}\phi_{\mathrm{B},0}} + \frac{a^2q^2}{18\phi_{\mathrm{B},0}}\right]^{-1} \tag{46}$$

$$S^0_{\mathrm{RR}}(q) = \left[\frac{1}{N_{\mathrm{R}}\phi_{\mathrm{R},0}} + \frac{a^2q^2}{18\phi_{\mathrm{R},0}}\right]^{-1} \tag{47}$$

and

$$\Delta = S^0_{\mathrm{AA}}(q) + S^0_{\mathrm{BB}}(q) + S^0_{\mathrm{RR}}(q) - \frac{1}{2}\chi_0 S^0_{\mathrm{AA}}(q)(S^0_{\mathrm{BB}}(q) + S^0_{\mathrm{RR}}(q)) - \frac{1}{2}\chi_0 S^0_{\mathrm{BB}}(q)(S^0_{\mathrm{AA}}(q) + S^0_{\mathrm{RR}}(q)) - \chi_0 S^0_{\mathrm{AA}}(q)S^0_{\mathrm{BB}}(q) \tag{48}$$

with χ_0 being the χ parameter before quench.

The time dependence of $S_{\mathrm{RR}}(q,t)$ can be obtained from

$$S_{\mathrm{RR}}(q,t) = S_{\mathrm{AA}}(q,t) + S_{\mathrm{BB}}(q,t) + 2S_{\mathrm{AB}}(q,t) \tag{49}$$

In the above discussion, we neglected the effects of thermal fluctuations. According to the generalized CHC

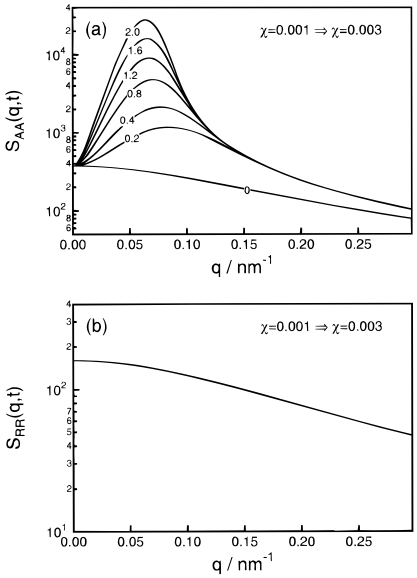

Figure 2. Time changes in $S_{AA}(q,t)$ (a) and $S_{RR}(q,t)$ (b) of the ternary system with $\phi_{R,0} = 0.20$ quenched from $\chi = 0.001$ to $\chi = 0.003$ or region II.

theory,[28,29] we obtain

$$S_{AA}(q,t) = \frac{1}{(\lambda_1(q) - \lambda_2(q))^2}[a_{T,1}(q)e^{2\lambda_1(q)t} + a_{T,2}(q)e^{(\lambda_1(q)+\lambda_2(q))t} + a_{T,3}(q)e^{2\lambda_2(q)t}] + S_{AA}(q,\infty) \quad (50)$$

$$S_{BB}(q,t) = \frac{1}{(\lambda_1(q) - \lambda_2(q))^2}[b_{T,1}(q)e^{2\lambda_1(q)t} + b_{T,2}(q)e^{(\lambda_1(q)+\lambda_2(q))t} + b_{T,3}(q)e^{2\lambda(q)_2t}] + S_{BB}(q,\infty) \quad (51)$$

and

$$S_{AB}(q,t) = \frac{1}{(\lambda_1(q) - \lambda_2(q))^2}[c_{T,1}(q)e^{2\lambda_1(q)t} + c_{T,2}(q)e^{(\lambda_1(q)+\lambda_2(q))t} + c_{T,3}(q)e^{2\lambda(q)_2t}] + S_{AB}(q,\infty) \quad (52)$$

where $S_{ij}(q,\infty)$ is the virtual structure factor given by eqs 42−48 in which χ_0 should be replaced by the χ parameter χ_T at a phase separation temperature T. The quantities of $a_{T,k}(q)$, $b_{T,k}(q)$, and $c_{T,k}(q)$ in eqs 50−52 are, respectively, $a_k(q)$, $b_k(q)$, and $c_k(q)$ in eqs 31−39, where $S_{ij}(q,0)$ values are replaced by $S_{ij}(q,0) - S_{ij}(q,\infty)$.

In the next section, we will calculate the time dependence of the structure factors of the ternary mixture quenched under different conditions.

III. Time Changes in the Structure Factors of the Ternary Systems

Here let us calculate the dynamics of the system with $N_A = N_B = N_R$. The parameters chosen are $N_A = N_B = N_R = 1000$, $D_A = D_B = D_R = 2000$ nm^2/s, and $a = 0.7$ nm. As the system discussed in the present paper satisfies the conditions with $N_A = N_B$ and $\phi_{A,0} = \phi_{B,0}$, $S_{AA}(q,t)$ and $S_{BB}(q,t)$ become identical. We, hence, investigate the time dependence of $S_{AA}(q,t)$ and $S_{RR}(q,t)$.

A. Quench into Region II. Figure 2 shows the time dependence of $S_{AA}(q,t)$ of the system with $\phi_{R,0} = 0.2$ quenched from $\chi = 0.001$ ($\chi N = 1$) to $\chi = 0.003$ ($\chi N = 3$) or Region II (point D in Figure 1b). This quench to region II causes two-phase separation and ϕ values of each equilibrium phase (points E and F in Figure 1b) are 0.663, 0.137, 0.2 and 0.137, 0.663, 0.2. In the time dependence of $S_{AA}(q,t)$, the peak appears at $q = 0.09$ nm^{-1} and the peak shifts to smaller q values. This tendency is similar to that of binary homopolymer blends. It is interesting to note that $S_{RR}(q,t)$ does not change either with time as shown in Figure 2b or with χ. We will discuss the reasons below.

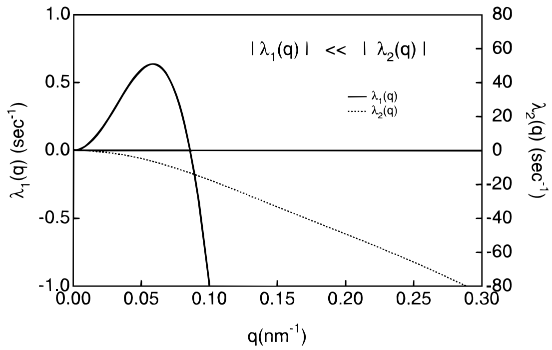

Figure 3. $\lambda_1(q)$ and $\lambda_2(q)$ plotted as a function of q for the ternary system with $\phi_{R,0} = 0.20$ quenched from $\chi = 0.001$ to $\chi = 0.003$ or region II.

Similarly to $S_{AA}(q,0)$ and $S_{BB}(q,0)$, $S_{RR}(q,0)$ is given by[25,26]

$$S_{RR}(q,0) = S^0_{RR}(q)[(S^0_{BB}(q) + S^0_{AA}(q)) - 2\chi_0 S^0_{AA}(q)S^0_{BB}(q)]/\Delta_R \quad (53)$$

with

$$\Delta_R = S^0_{RR}(q) + S^0_{AA}(q) + S^0_{BB}(q) - \frac{1}{2}\chi_0 S^0_{RR}(q)(S^0_{BB}(q) + S^0_{AA}(q)) - 2\chi_0 S^0_{AA}(q)S^0_{BB}(q) \quad (54)$$

Substituting the relation

$$S^0_{AA}(q) = S^0_{BB}(q) \quad (55)$$

into eqs 53 and 54 and rearranging eq 53, we obtain

$$S_{RR}(q,0) = \frac{2S^0_{RR}(q)S^0_{AA}(q)}{S^0_{RR}(q) + 2S^0_{AA}(q)} = S_{RR}(q,\infty) \quad (56)$$

Thus, we find that $S_{RR}(q,0)$ and $S_{RR}(q,\infty)$ are independent of χ. By substituting $S_{RR}(q,0) = S_{RR}(q,\infty)$ into eqs 49 and 50−52, we obtain

$$S_{RR}(q,t) = S_{RR}(q,\infty) \quad (57)$$

so that $S_{RR}(q,t)$ becomes constant with time within the frame of CHC theory. This feature in $S_{RR}(q,t)$ is common in all regions so that we do not show the time dependence of $S_{RR}(q,t)$ later.

In Figure 3, $\lambda_1(q)$ and $\lambda_2(q)$ are plotted as a function of q. It is found that $\lambda_2(q)$ is negative at all q regions and that $|\lambda_1(q)|$ is smaller than $|\lambda_2(q)|$ at all q regions. These features indicate that the time dependence of $S_{AA}(q,t)$ at longer times can be described by

$$S_{AA}(q,t) \cong \frac{a_{T,1}(q)e^{2\lambda_1(q)t}}{(\lambda_1(q) - \lambda_2(q))^2} + S_{AA}(q,\infty) \quad (58)$$

which is similar to the CHC type equation for the time evolution of the structure factor in homopolymer blends.[16]

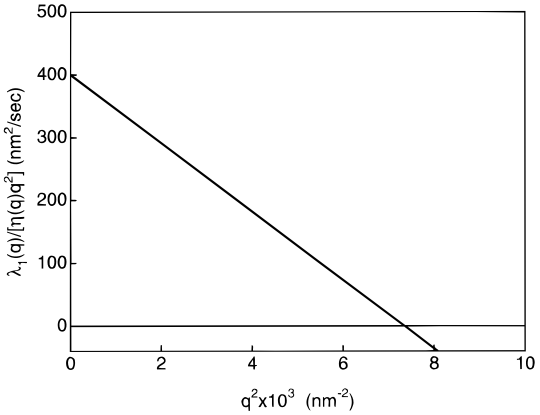

Figure 4. Plot of $\lambda_1(q)/[\eta(q)/q^2]$ for the ternary system with $\phi_{R,0} = 0.20$ quenched from $\chi = 0.001$ to $\chi = 0.003$ or region II.

Figure 4 is the so-called "Cahn plot" for $\lambda_1(q)$, i.e., $\lambda_1(q)/[\eta(q)q^2]$ vs q^2 plot, where $\eta(q)$ is given by

$$\eta(q) = [1 - \exp(-N_k a^2 q^2/6)]/N_k a^2 q^2 \qquad (59)$$

It is noted that we divided $\lambda_1(q)/q^2$ by $\eta(q)$ to remove the q dependence of $\Lambda_{AA}(q)$ from the plot. The plot shows linearity between $\lambda_1(q)/[\eta(q)q^2]$ and q^2 so that the characteristic parameters, the mutual diffusion coefficient D_{app} and the wavenumber $q_m(0)$, can be obtained from Figure 4. The values of D_{app} and $q_m(0)$ are 400 nm^2/s and 0.06 nm^{-1}, respectively.

Let us consider the quantities of $\lambda_1(q)$ with the conditions $N_A = N_B$ and $\phi_{A,0} = \phi_{B,0}$. Under these conditions, $D_{ij}(q)$ values in eqs 24−27 satisfy

$$D_{11}(q) = D_{22}(q) \qquad (60)$$

and

$$D_{12}(q) = D_{21}(q) \qquad (61)$$

The solutions $\lambda_1(q)$and $\lambda_2(q)$ of eq 41, hence, are

$$\lambda_1(q) = (-\Lambda_{AA} + \Lambda_{AB})q^2\left[\frac{1}{N_H\phi_{H,0}} - \chi + \frac{a^2}{18\phi_{H,0}}q^2\right] \qquad (62)$$

and

$$\lambda_2(q) = -(\Lambda_{AA} + \Lambda_{AB})q^2\left[\frac{1}{N_H\phi_{H,0}} + \frac{2}{N_H\phi_{H,0}} + \left(\frac{a^2}{18\phi_{H,0}} + \frac{2a^2}{18\phi_{R,0}}\right)q^2\right] \qquad (63)$$

where $N_H = N_A = N_B$ and $\phi_{H,0} = \phi_{A,0} = \phi_{B,0}$. As seen in eq 62, the concentration fluctuation becomes unstable at $q < q_c$ when χ becomes greater than a critical point for two-phase separation at this composition [$=1/(N_H\phi_{H,0})$], where q_c is given by

$$q_c = \left[\frac{18}{N_H a^2}\frac{\chi - \chi_c}{\chi_c}\right]^{1/2} \qquad (64)$$

with

$$\chi_c = \frac{1}{N_H\phi_{H,0}} \qquad (65)$$

Equations 64 and 65 indicate that the instability of the concentration fluctuations depends on the quench depth or $(\chi - \chi_c)$ and are independent of the tricritical point of the blends. This equation is similar to the growth rate for binary homopolymer blends. Actually, if we neglect the term of the random copolymer, $\lambda_1(q)$ becomes identical with the expression of growth rate for binary homopolymer blends composed of A and B. This means that this $\lambda_1(q)$ mode represents the dynamics of the concentration fluctuations caused by the interdiffusion between homopolymer A and homopolymer B. On the other hand, $\lambda_2(q)$ is found to be independent of χ. This mode corresponds to the dynamics of the interdiffusion between the random copolymer and homopolymer A or B. For such a symmetric case, the random copolymer acts as a Θ solvent for both homopolymers so that the concentration fluctuations of the random copolymer tend to maintain a homogeneous state as indicated in the expression of $\lambda_2(q)$.

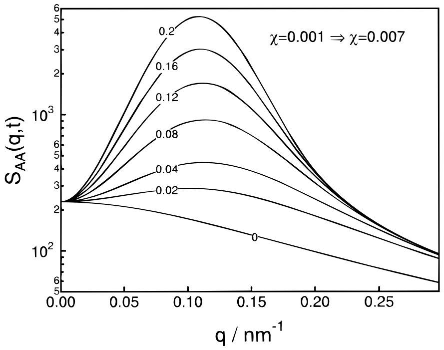

Figure 5. Time change in $S_{AA}(q,t)$ of the ternary system with $\phi_{R,0} = 0.5$ quenched from $\chi = 0.001$ to $\chi = 0.007$ or region III.

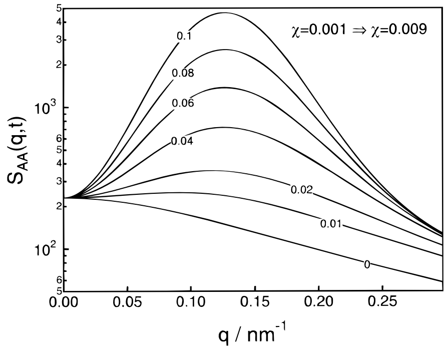

Figure 6. Time change in $S_{AA}(q,t)$ of the ternary system with $\phi_{R,0} = 0.5$ quenched from $\chi = 0.001$ to $\chi = 0.009$ or region IV.

B. Quench into Regions III and IV. Figures 5 and 6 show the time dependence of $S_{AA}(q,t)$ of the system with $\phi_{R,0} = 0.5$ quenched from $\chi = 0.001$ ($\chi N = 1$) to $\chi = 0.007$ ($\chi N = 7$) or region III (point G in Figure 1c) and $\chi = 0.009$ ($\chi N = 9$) or region IV (point M in Figure 1d), respectively. Under these quench conditions, the mixture separates into three phases and ϕ values of each equilibrium phase are 0.140, 0.140, 0.720 (point H in Figure 1c), 0.584, 0.010, 0.406 (point I in Figure 1c), and 0.010, 0.584, 0.406 (point J in Figure 1c), for the quench to $\chi N = 7$, and 0.0930, 0.0930, 0.814 (point N in Figure 1d), 0.8195, 0.0005, 0.1800 (point O in Figure 1d), and 0.0005, 0.8195, 0.1800 (point P in Figure 1d), for the quench to $\chi N = 9$. Similarly to the case quenched into region II, it is shown that the peak appears and shifts to smaller q values in $S_{AA}(q,t)$ as shown in Figure 2a. Figures 7 and 8 illustrate the q dependence of $\lambda_1(q)$ and $\lambda_2(q)$ and the Cahn plot for $\lambda_1(q)$ for the quench to regions III and IV, respectively. Again, we found that the plots of $\lambda_1(q)/[\eta(q)q^2]$ and q^2 become linear in Figures 7b and 8b as in Figure 4. The

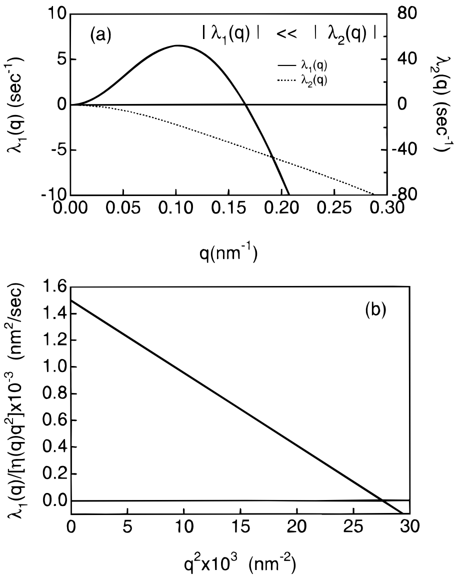

Figure 7. $\lambda_1(q)$ and $\lambda_2(q)$ vs q (a) and the plot of $\lambda_1(q)/[\eta(q)/q^2]$ for the quench to $\chi = 0.007$ or region III.

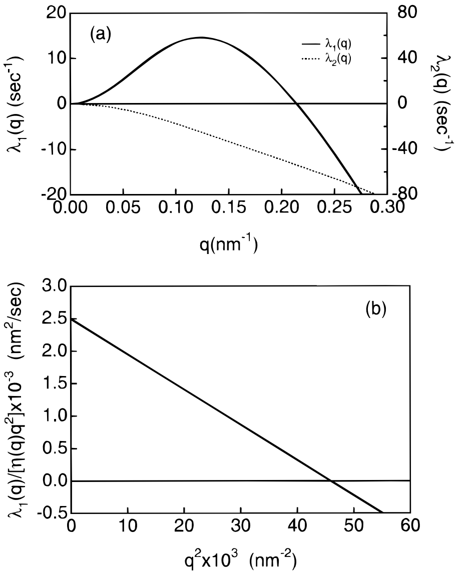

Figure 8. $\lambda_1(q)$ and $\lambda_2(q)$ vs q (a) and the plot of $\lambda_1(q)/[\eta(q)/q^2]$ for the quench to $\chi = 0.009$ or region IV.

reason for the similarity between the dynamics of early-stage SD in region II and those in regions III and IV is that the growth mode $\lambda_1(q)$ depends on $(\chi - \chi_c)$ as described before.

IV. Conclusions

We have formulated the CHC theory describing the dynamics of early-stage SD in a ternary mixture composed of homopolymers and a random copolymer within the Flory–Huggins theory. We adopted both the slow theory and the fast theory to the CHC theory. We calculated the dynamics of the structure factors of the system in which each component has an identical polymerization index and the space-averaged volume fractions of homopolymers are equal. The analyses revealed the following points. The time dependence of the structure factors for a component polymer (e.g. A) in the ternary mixtures quenched into region II (two-phase region) was identical to that quenched into region III or IV (three-phase region). They were all similar also to that of binary homopolymer blends. This similarity is because (i) the dominant growth mode $\lambda_1(q)$ due to the interdiffusion between homopolymer A and homopolymer B is similar to the expression of the growth rate of binary homopolymer blends and (ii) the random copolymer acts as a Θ solvent for both components and tends to spread homogeneously. The second feature (ii) holds in the whole time scale in the context of the linearized theory. In the context of CHC theory, the higher order (or nonlinear term) of the concentration fluctuations in the chemical potential has been neglected. The difference between the dynamics above the tricritical point (region II) and those below the tricritical point (regions III and IV), hence, would appear in the later stage where the nonlinear term becomes important in the dynamics of the concentration fluctuations. Recently, we have reported preliminary results on the later stage dynamics of the mixture with computer simulation where the nonlinear term was included in the chemical potential; we found that the mixture quenched under the tricritical point underwent three-phase separation consisting of A-rich, B-rich, and A-r-B-rich regions.[30] We will investigate the dynamics of the mixture quenched above the tricritical point and explore the difference in a future publication.[31]

Appendix

Here let us calculate the Onsager kinetic coefficient Λ_{ij} by using both the slow theory and the fast theory. According to the de Gennes procedure (or the slow theory), the flux is described by

$$\mathbf{J}_{\mathrm{A}} = -\Lambda_{0,\mathrm{AA}} \nabla(\mu_{\mathrm{A}} + U) \tag{A.1}$$

$$\mathbf{J}_{\mathrm{B}} = -\Lambda_{0,\mathrm{RR}} \nabla(\mu_{\mathrm{R}} + U) \tag{A.2}$$

and

$$\mathbf{J}_{\mathrm{R}} = -\Lambda_{0,\mathrm{RR}} \nabla(\mu_{\mathrm{R}} + U) \tag{A.3}$$

where U is the potential determined by the incompressible condition. $\Lambda_{0,kk}$ is given by eq 18. The incompressible condition

$$\mathbf{J}_{\mathrm{A}} + \mathbf{J}_{\mathrm{B}} + \mathbf{J}_{\mathrm{R}} = 0 \tag{A.4}$$

leads to ∇U

$$\nabla U = -\frac{\Lambda_{0,\mathrm{AA}}\nabla\mu_{\mathrm{A}} + \Lambda_{0,\mathrm{BB}}\nabla\mu_{\mathrm{B}} + \Lambda_{0,\mathrm{RR}}\nabla\mu_{\mathrm{R}}}{\Lambda_{0,\mathrm{AA}} + \Lambda_{0,\mathrm{BB}} + \Lambda_{0,\mathrm{RR}}} \tag{A.5}$$

Substituting eq A.5 into eqs A.1 and A.2 and rearranging eqs A.1 and A.2, we then have

$$\mathbf{J}_{\mathrm{A}} = -\frac{\Lambda_{0,\mathrm{AA}}(\Lambda_{0,\mathrm{BB}} + \Lambda_{0,\mathrm{RR}})}{\sum_{k=\mathrm{A,B,R}} \Lambda_{0,kk}} \nabla(\mu_{\mathrm{A}} - \mu_{\mathrm{R}}) - \frac{-\Lambda_{0,\mathrm{AA}}\Lambda_{0,\mathrm{BB}}}{\sum_{k=\mathrm{A,B,R}} \Lambda_{0,kk}} \nabla(\mu_{\mathrm{B}} - \mu_{\mathrm{R}}) \tag{A.6}$$

and

$$\mathbf{J}_\mathrm{B} = -\frac{-\Lambda_{0,\mathrm{AA}}\Lambda_{0,\mathrm{BB}}}{\sum_{k=\mathrm{A,B,R}}\Lambda_{0,kk}}\nabla(\mu_\mathrm{A}-\mu_\mathrm{R}) - \frac{\Lambda_{0,\mathrm{BB}}(\Lambda_{0,\mathrm{AA}}+\Lambda_{0,\mathrm{RR}})}{\sum_{k=\mathrm{A,B,R}}\Lambda_{0,kk}}\nabla(\mu_\mathrm{B}-\mu_\mathrm{R}) \quad (\mathrm{A.7})$$

A comparison between eqs A.6 and A.7 and eqs 4 and 5 gives eqs 15−17.

On the other hand, Brochard proposed the tube velocity concept and derived the following equations:

$$\mathbf{J}_\mathrm{A} = -\Lambda_{0,\mathrm{AA}}\nabla\mu_\mathrm{A} + \phi_\mathrm{A}v_T \quad (\mathrm{A.8})$$

$$\mathbf{J}_\mathrm{B} = -\Lambda_{0,\mathrm{BB}}\nabla\mu_\mathrm{B} + \phi_\mathrm{B}v_T \quad (\mathrm{A.9})$$

and

$$\mathbf{J}_\mathrm{R} = -\Lambda_{0,\mathrm{RR}}\nabla\mu_\mathrm{R} + \phi_\mathrm{R}v_T \quad (\mathrm{A.10})$$

where v_T is the tube velocity of the system given by

$$v_T = \Lambda_{0,\mathrm{AA}}\nabla\mu_\mathrm{A} + \Lambda_{0,\mathrm{BB}}\nabla\mu_\mathrm{B} + \Lambda_{0,\mathrm{RR}}\nabla\mu_\mathrm{R} \quad (\mathrm{A.11})$$

Substituting eq A.11 into eqs A.8 and A.9, we obtain

$$\mathbf{J}_\mathrm{A} = -\Lambda_{0,\mathrm{AA}}\nabla\mu_\mathrm{A} + \phi_\mathrm{A}(\Lambda_{0,\mathrm{AA}}\nabla\mu_\mathrm{A} + \Lambda_{0,\mathrm{BB}}\nabla\mu_\mathrm{B} + \Lambda_{0,\mathrm{RR}}\nabla\mu_\mathrm{R}) \quad (\mathrm{A.12})$$

and

$$\mathbf{J}_\mathrm{B} = -\Lambda_{0,\mathrm{BB}}\nabla\mu_\mathrm{B} + \phi_\mathrm{B}(\Lambda_{0,\mathrm{AA}}\nabla\mu_\mathrm{A} + \Lambda_{0,\mathrm{BB}}\nabla\mu_\mathrm{B} + \Lambda_{0,\mathrm{RR}}\nabla\mu_\mathrm{R}) \quad (\mathrm{A.13})$$

By using the Gibbs−Duhem relation, eqs A.12 and A.13 can be simplified to

$$\mathbf{J}_\mathrm{A} = -\{(1-\phi_\mathrm{A})^2\Lambda_{0,\mathrm{AA}} + \phi_\mathrm{A}^2\Lambda_{0,\mathrm{BB}} + \phi_\mathrm{A}^2\Lambda_{0,\mathrm{RR}}\}\nabla(\mu_\mathrm{A} - \mu_\mathrm{R}) - \{-(1-\phi_\mathrm{A})\phi_\mathrm{B}\Lambda_{0,\mathrm{AA}} - \phi_\mathrm{A}(1-\phi_\mathrm{B})\Lambda_{0,\mathrm{BB}} + \phi_\mathrm{A}\phi_\mathrm{B}\Lambda_{0,\mathrm{RR}}\}\nabla(\mu_\mathrm{B}-\mu_\mathrm{R}) \quad (\mathrm{A.14})$$

and

$$\mathbf{J}_\mathrm{B} = -\{-\phi_\mathrm{A}(1-\phi_\mathrm{B})\Lambda_{0,\mathrm{AA}} - (1-\phi_\mathrm{B})\phi_\mathrm{A}\Lambda_{0,\mathrm{BB}} + \phi_\mathrm{A}\phi_\mathrm{B}\Lambda_{0,\mathrm{RR}}\}\nabla(\mu_\mathrm{A}-\mu_\mathrm{R}) - \{\phi_\mathrm{B}^2\Lambda_{0,\mathrm{AA}} + (1-\phi_\mathrm{B})^2\Lambda_{0,\mathrm{BB}} + \phi_\mathrm{B}^2\Lambda_{0,\mathrm{RR}}\}\nabla(\mu_\mathrm{B}-\mu_\mathrm{R}) \quad (\mathrm{A.15})$$

respectively. A comparison between eqs A.14 and A.15 and eqs 4 and 5 gives eqs 19−21.

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